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Photochemistry of Nitrous Acid in Benzene

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PHOTOCHEMISTRY OF NITROUS ACID IN BENZENE

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Nitrous acid is thought to have an important role in atmospheric pollution. It absorbs long wavelength ultraviolet light efficiently and undergoes photochemical reactions to produce hydroxyl radical, which contributes to smog formation and ozone depletion.

Photolysis of the aqueous nitrous acid/nitrite ion system at 366 nm results in the formation of hydroxyl radical and nitric oxide. The relative contributions of radicals from the molecular and ionic forms is unknown. This study is intended to concentrate upon the contribution of radicals from molecular nitrous acid.

The photochemistry of nitrous acid is studied in benzene in order to eliminate the contribution from nitrite ion which is insoluble in benzene. An added benefit of benzene is its ability to scavenge the radicals, to form the products phenol and paranitrosophenol, which can be observed using UV-Vis spectroscopy. Without this scavenging reaction, direct observation of hydroxyl radical is difficult.

Thermal reaction of nitrous acid in benzene has been observed to occur at room temperature. The rate of this reaction is significant and must be accounted for in quantifying the photochemical reaction. The reaction solutions were cooled to 5°C to decrease the rate of thermal reaction.

Photolysis of nitrous acid in benzene with 366 nm mercury lamps has been shown to cause a loss of the reactant nitrous acid by disappearance of the characteristic peak absorbances in the ultraviolet spectrum. Also, peaks which may correspond to the products have been observed growing into the UV. These peaks occur at 300 nm which is where phenol and paranitrosophenol are known to absorb in the UV.